THE CONTROVERSY OF YOUNG VS. OLD AGE OF FORMATION OF CARBONATES IN ALH84001.

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The ALH84001 meteorite is unusual among the SNC (martian) meteorites not only because it has a significantly old crystallization age of ~4.5 Ga [1,2], but also because it contains abundant carbonates (~1 vol. %) which are believed to have formed from interaction with a CO_2-rich fluid phase in a near-surface environment on Mars [3,4,5,6]. Recently it has been suggested that these carbonates may contain evidence of past biogenic activity on Mars [7]. In their study, McKay et al. [7] adopted a 3.6 Ga age for these carbonates, which was obtained by the Ar-Ar laser probe technique [8]. As indicated by [7], this relatively old age makes the interpretation of the observed microstructures within these carbonates as "nanofossils" more likely, since at that time climatic conditions on Mars may have been similar to those on the early Earth (i.e., significantly warmer and wetter than at later times in the geologic history of that planet) making it possible for primitive (bacterial?) life to thrive. However, the 3.6 Ga age for the carbonates as reported by [8] is subject to considerable uncertainties, since the K- and Ar-bearing phase that was analysed was not the carbonate, but rather the maskelynite which is closely associated with it [9]. Therefore, the suggested 3.6 Ga age is wholly dependent on whether or not the maskelynite was completely degassed by interaction with the fluid that deposited the carbonates, further requiring that these carbonates be deposited at high temperature. However, at present, there is no consensus on the issue of the temperature of the fluid that precipitated the carbonates (see LPSC XXVIII abstracts volume).

Last year we reported the initial findings of our study of the Rb-Sr systematics in ALH84001 [10]. Here we further discuss the implications for the age of carbonates based on these data. The figure shows a plot of the Sr isotopic ratios vs. the Rb/Sr ratios for the analysed mineral separates and bulk samples of ALH84001. It is evident from this figure that data for the bulk samples, TR1 and TR2, as well as for the pyroxene separates, Px(a) and Px(b), fall on a best fit line corresponding to an "age" of 3.84 ± 0.05 billion years, which is considerably lower than what was reported by [2]. (The reason for the severe discrepancy between the Rb-Sr age determined by us and that reported by [2] is not clear. However, it may be that the "plag" data point of [2], which, unlike most common plagioclase compositions, is the most radiogenic data point reported by these authors, may not represent a pure plagioclase separate. This is supported by *in situ* ion microprobe analyses of Rb/Sr ratios in maskelynite, indicated by the shaded zone in the figure, which show a much lower Rb/Sr ratio than that reported by [2]) Our "age" recorded by the Rb-Sr system is similar to the Ar-Ar shock age reported by [11] and, therefore, most likely reflects the time of intense shock experienced by ALH84001. It should be further noted that while TR1 was only ~3 mg, the TR2 sample was ~100 mg and, thus, is presumably representative of the true whole rock. This is important because the 4.56 billion year reference isochron passes through the TR2 data point and this is wholly consistent with the initial formation of ALH84001 4.56 billion years ago with an initial $^{87}Sr/^{86}Sr$ = 0.69897, followed by re-equilibration of the Rb-Sr system 3.84 billion years ago, resulting in $I(^{87}Sr/^{86}Sr)$ = 0.70215 at that time.

Another feature evident in the figure is that the plagioclase data points, Pl(a) and Pl(b), as well as the carbonate data point, C(b) do not fall on the 3.84 Ga isochron defined by the bulk samples and pyroxene separates. Both plagioclase data points fall to the right, while the carbonate data point falls to the left of the 3.84 Ga isochron. It is important to note that the Rb/Sr ratio of the Pl(b) data point falls well within the range of Rb/Sr ratios measured *in situ* by ion microprobe analyses of three plagioclase grains (unpubl. data) in a thin section of ALH84001, shown by the shaded region in the figure. This indicates that the Pl(b) data point most likely represents a pure plagioclase mineral separate, while the Pl(a) separate may have contained a small amount of a trace phase rich in Sr. Therefore, of the two plagioclase mineral separates, the Pl(b) data point most likely represents a pure plagioclase separate.

It is to be noted that chronologic information regarding carbonate formation derived from the Rb-Sr data obtained so far is dependent on the source of the Sr in the carbonates. There are three main possibilities, which are as follows: (i) A significant portion of the Sr is extraneously derived and has no relation to the host rock. In this case, no chronologic information can be derived from the data obtained. (ii) Sr is derived predominantly from the bulk meteorite. Assuming that TR2 is representative of the bulk sample (see above), a carbonate formation isochron can be drawn between the C(b) and TR2 data points. This would result in a carbonate formation age of 3.69 ± 0.06 Ga (see figure). (iii) Sr is derived predominantly from the maskelynitized plagioclase. A carbonate isochron between the C(b) and Pl(b) data points results in a formation age of 1.39 ± 0.10 Ga (see figure).

Of the above possibilities, case (i) is not favored since it requires ad hoc explanations for why TR1, TR2, Px(a) and Px(b) fall on a single Rb-Sr isochron, if the two bulk rock fractions indeed contain variable amounts of extraneous Sr contributed by the carbonate. Case (ii) is also unlikely since it cannot adequately explain why the bulk rock and pyroxene fractions define a good isochron but the plagioclase fraction clearly lies off it. In particular, for TR1 (small bulk rock fraction, which appears to be enriched in components that have the least radiogenic Sr, like plagioclase and carbonates) to lie on the 3.84 Ga isochron requires fortuitously correct proportions of plagioclase and carbonate. This is highly unlikely unless the plagioclase and carbonates are closely associated, as would indeed be the case if the Sr in the carbonate is largely derived from the plagioclase, i.e., case (iii). Case (iii) is additionally favored by (1) the close and "symmetric" (with respect to the 3.84 Ga isochron) association of the Pl(b) and C(b) data points (see figure), and (2) the *predominant* spatial association of the carbonates with the plagioclase, as noted by several authors [3,5,6]. Although some small carbonate grains have been found in apparent association with other phases [6], we have observed this to occur mainly in crushed domains indicating transport of these carbonates from their original site of formation. Therefore, it seems *most likely* that the formation age of the carbonates in ALH84001 is 1.39 ± 0.10 Ga. We note that if this 1.39 Ga formation age for the carbonates is indeed true, the interpretation of the microstructures observed by [7] as fossilized ancient martian nanobacteria becomes less likely since the martian climatic conditions at this more recent time may not have been conducive to life.

From the above, the relatively young formation age of the carbonates is a likely possibility. However, to unequivocally confirm this finding we have begun an attempt to measure single carbonate and plagioclase grains which are found in true association with one another.

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